

EFFECTS OF OXYGEN PARTIAL PRESSURE ON FUEL CELL CATHODES

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INTRODUCTION

The study of transport and electrochemical processes occurring at the oxygen cathode is of fundamental importance in fuel cell development. The oxygen depolarized cathode is the major determining factor for cell efficiency in H_2 /Air fuel cells. It becomes important then to investigate this factor since the oxygen depolarized cathode is common to all fuel/air cells. Additional value may be derived from this study since the investigation of the transport processes occurring at the oxygen cathode would afford an insight into the processes occurring at anodes using insoluble fuels and exhibiting activation polarization.

In order to obtain larger practical current densities, it is necessary to provide a large reaction zone for apparent electrode area. This is usually accomplished by employing porous electrodes having a high ratio of reaction area to apparent electrode area. The liquid electrolyte would then partially permeate the pores of the electrode and the balancing gas pressure on the reverse side of the cathode establishes a liquid meniscus of a three-phase (electrode/oxidant/electrode) interface.

During this study, the three-phase interface was produced by partly immersing a flat-plate cathode into the electrolyte. This arrangement was preferred because of two inherent difficulties associated with porous matrices, namely; poor reproducibility, and the difficulty in accurately defining the reaction zone. The effects of p_{O_2} up to 10 atm on the current-voltage characteristics of these complex porous structures compared favorably with results obtained with flat-plate electrodes. The materials used for the flat-plate electrodes were Pt, Au, Ag and Pd.

Experimental. The experimental arrangement used is shown in Figure 1. Standard potential-current measurements were made in the p_{O_2} range 0.10 to 10 atm. A Wenking potentiostat was used for the series of experiments when the potential was maintained constant. In order to eliminate any slight current contributions that would arise from the electrode portion immersed in the electrolyte, the data reported herein were obtained with the electrode entering at the surface of the electrolyte. The results indicate that the bulk of the current is generated in a zone near the meniscus or three-phase interface as also reported by Sama et al ¹ and Will ².

The difficulty in defining the three-phase interface is complicated by the presence of oxides and uneven surfaces. For this reason we obtain reproducible current densities by expressing them in μA per linear centimeter of the interface. In order to prevent disturbance of the interface, the electrolyte was not stirred while measurements were taken.

EFFECT OF p_{O_2} ON OCV AND POLARIZATION

Results and Discussion. As shown in Figure 2, the partial pressure of oxygen affects both the OCV and potential at constant current. Although changes in OCV are anticipated in accordance with the Nernst equation, the changes in the potential at constant current merit closer examination. It can be readily seen from Figure 2 that potentials at constant current become more anodic with increasing p_{O_2} and that polarization decreases as the p_{O_2} increases. However, this polarization decrease becomes less rapid as p_{O_2} rises.

A better understanding of the diminishing effect of p_{O_2} on polarization can be derived when p_{O_2} or $\log p_{O_2}$ values are plotted vs. polarization at constant current density (see Figures 3 and 4).

According to Weber, Meissner and Sama¹ the rate limiting step for a partially immersed depolarized oxygen cathode is mass transport of oxygen through the liquid meniscus zone. Since p_{O_2} is a major mass transport parameter our studies were extended to partial pressures of oxygen ≤ 10 atm to study its effect.

It is evident from our studies that p_{O_2} has a decided effect on the polarization of the electrodes and that the p_{O_2} polarization relationship is not linear. The current (i) obtainable from the transport of oxygen through an electrolyte layer can be expressed by the following equation,³

$$i_C = DZF(C_1 - C_2) / \delta \quad (1)$$

where: D = the diffusion coefficient

C_1 = concentration of O_2 at the gas/liquid interface

C_2 = concentration of O_2 at the electrode surface

δ = thickness of the diffusion layer

Z = no. of electrons transferred during the reaction

F = the Faraday constant

$$\text{For a limiting current } (i_1), C_2 = 0 \text{ and } i_1 = DZF(C) / \delta \quad (2)$$

The relationship for concentration polarization (η_C) is:

$$\eta_C = (2.303 RT/ZF) \log i_1 \left(\frac{i_1}{i_1 - i_C} \right) \quad (3)$$

where: R = the Ideal Gas Constant

T = Temperature, $^{\circ}K$

i_C = the current obtained at η_C

According to equation 3, a drop in concentration polarization may be obtained by increasing limiting current. Equation 2 implies that this can be accomplished by:

- Increasing D (i.e., increasing temperature).
- Decreasing δ (through agitation).
- Increasing C_1

D and δ were kept constant in our experiments by maintaining constant temperature and preventing agitation of the electrolyte.

By substituting equations 1 and 2 in 3

$$\eta_C = (2.303 RT/ZF) \log \left(\frac{DZFC_1/\delta}{DZFC_1/\delta - DZF(C_1 - C_2/\delta)} \right)$$

At constant current, $(C_1 - C_2)$ will be constant, i. e., equal to K_1 . Then

$$\eta_C = (2.303 RT/ZF) \log \left(\frac{C_1}{C_1 - K_1} \right)$$

The concentration of oxygen at the gas/liquid interface C_1 is a function of p_{O_2} . Therefore,

$$\eta_C = \frac{2.303 RT}{ZF} \log \left[\frac{f(p_{O_2})}{f(p_{O_2}) - K_1} \right]$$

where $\lim p_{O_2} = \infty$

$f(p_{O_2}) \rightarrow \infty$. According to this relationship, for a given current:

- a. $\lim \eta_C = 0$
 $f(p_{O_2}) \rightarrow \infty$
- b. $\lim \eta_C = \infty$
 $f(p_{O_2}) \rightarrow K_1$.

This has been confirmed by experimental data.

Our experimental results show that highly active porous structures having a three-phase interface exhibit the same sensitivity to p_{O_2} as the flat-plate cathodes (see Figures 5 and 6).

These results also illustrate the limitation imposed by oxygen mass transport through an electrolyte layer. This is significant because although the flat-plate cathode may be considered as an idealized model of a porous structure, the same limiting process (oxygen mass transfer through the electrolyte meniscus) occurs for both electrode types. Therefore, the flat-plate "model" electrode system is directly applicable to a porous electrode for purposes of comparison of p_{O_2} effects.

Equipotential Current. It has been observed that at -0.8 volt from OCV, the four catalysts tested (Pt, Pd, Ag, and Au) yielded identical currents on flat-plate electrodes. This reference potential (-0.8 V) was chosen because a true limiting current could not be obtained before reaching the H_2 -deposition region. The maximum obtainable current (i_E) refers to the current produced per cm length of meniscus at -0.8 volt polarization vs. OCV.

EFFECT OF p_{O_2} ON "MAXIMUM CURRENT"

In the initial experiments, p_{O_2} was varied and the corresponding i_E values were observed. The $i_E - p_{O_2}$ data obtained were plotted using log coordinates (see Figure 5, curve 2). It can be seen from this curve that i_E is independent of the catalytic material and varies with $(p_{O_2})^{1/2}$, i. e., $i_E = A \log p_{O_2} + B$, where the constant A is 0.5 (calculated) and the constant B approximately equals 740 μA per cm length of meniscus on the flat-plate cathodes. This relationship enables prediction of i_E at any p_{O_2} within the range studied

by the equation:

$$\frac{i_{E,1}}{i_{E,2}} = \left(\frac{p_{O_2,1}}{p_{O_2,2}} \right)^{1/2} \quad (4)$$

where $i_{E,1}$ and $i_{E,2}$ are the maximum currents obtainable for a flat-plate cathode in the same electrolyte concentration at $p_{O_2,1}$ and $p_{O_2,2}$, respectively. From the above data it could be safely concluded that either the four metals tested have identical catalytic activity, which is unlikely, or that under the experimental conditions (800 mV polarization from the rest potential), the catalytic activity no longer has a significant effect on the current. This is explainable since at potentials 800 mV from the rest potential, the electrochemical reaction is no longer rate controlling, and its effect is masked. Figure 5, line 1 is a log plot of the results obtained using a porous structure with negligible activation polarization. It can be seen that with this structure, the currents obtained at equal polarization also vary with $(p_{O_2})^{1/2}$.

Oxygen Transport. When it was established that the catalytic activity of the electrode was not a current controlling factor, attention was then focused on other possible factors such as mass transport of oxygen to the catalytic sites. Sama, et al.¹ reported, that the bulk of the current obtained from a half immersed flat-plate electrode, was generated near the immediate vicinity of the triple interface. It was also established that oxygen is transported to the catalytic sites through the electrolyte.

There are two possible rate-controlling steps in such a case. One is liquid phase diffusion of dissolved oxygen, the other is interphase mass transfer of oxygen from the gas into the liquid phase. Should ordinary diffusion in the liquid phase be the rate controlling step, and the liquid surface in contact with the gas is saturated with oxygen, then a linear variation of current with p_{O_2} would occur.

Investigating the case where liquid phase diffusion could be the only possible rate controlling factor, Reti⁵ performed an experiment, in the course of which he pre-saturated electrolytes with O_2 at various partial pressures. He then pumped the electrolytes through silver or platinum screen electrodes. Under constant hydrodynamic conditions, (flow rate and temperature), he found a linear relationship between equipotential currents and the partial pressure of oxygen in the pre-saturating gas. Higher currents therefore can be obtained for a given p_{O_2} if pre-saturated electrolyte is used.

If ordinary linear diffusion was the mass transfer controlling step under the experimental conditions of our study then p_{O_2} would exhibit a linear relationship with current. Our experimental data show that $i_E \propto (p_{O_2})^{1/2}$, which would appear to eliminate the possibility of ordinary diffusion being a mass transfer controlling step.

Effect of O_2 Solubility on i_E . The curves in Figure 8 were plotted from i_E vs. electrolyte molar concentration data which were obtained to determine the effects of O_2 solubility on i_E . If equation 4 is valid at all concentrations then the maximum current obtainable at any p_{O_2} can be predicted from the actual data measured at any other p_{O_2} at the same KOH concentration. For example (refer to Figure 8), if the calculations are based on data at $p_{O_2} = 1$ atm, the predicted (dotted line) and experimental (solid line) values at $p_{O_2} = 0.6$ atm and 0.21 atm are in close agreement.

Studies were made of the currents obtained at various electrolyte concentrations in which the equilibrium concentration of O_2 in the electrolyte was kept constant (by adjusting p_{O_2}).

As seen in Table 1 (similar plot as Figure 8), at equal equilibrium concentrations of O_2 in KOH at a given p_{O_2} (C^*), the currents obtained are approximately equal. Because data for solubility of O_2 in KOH is very limited in the literature, extrapolations had to be made at several points to obtain the solubility value. Thus, because of the lack of solubility data, the actual KOH molar concentrations at which C^* values are equal at different p_{O_2} values cannot be accurately predicted. According to the data shown in Figure 7, i_E varied with $(p_{O_2})^{1/2}$. It is well known that in the case of transport of a slightly soluble gas into a liquid, the bulk of the resistance is in the liquid phase. Due to this limitation the bulk liquid near the transfer zone is not reaching the equilibrium saturation as predicted using Henry's law. If we plot i_E vs. the equilibrium solubility of oxygen (C^*) at various electrolyte concentrations we obtain a relationship similar to the one previously shown, that is $i_E = A' \log C^* + B$ where the experimentally obtained A' value is 0.48, which compares well with the previously obtained 0.5 value (see Figure 9). Use of extrapolated C^* values due to the scarcity of actual solubility data in the literature may be used to account for this deviation.

TABLE 1
 i_E OBTAINED FOR VARIOUS C^* VALUES
IN KOH ELECTROLYTE

$C_{KOH} = 1M$			$p_{O_2} = 1 \text{ atm}$		
p_{O_2} (atm)	C^* (ml/l)	i_E ($\mu A/cm^\ddagger$)	C_{KOH} (M)	C^* (ml/l)	i_E ($\mu A/cm^\ddagger$)
1	22.2	1320	-	-	-
0.6	13.32	1008	2.18	13.32	1130
0.21	4.66	685	5.5	4.66	700

\ddagger Length of meniscus

Note- Electrode: Polished Flat Gold-Plate Cathode
Temperature: 25°C

The current-partial pressure relationship developed earlier in this paper (see equation 4), can be used to predict electrode polarization when $E-i$ curves are linear. This is the case, for example, for the highly active complex porous electrode structures shown in curve 1 of figure 7.

If the slope of the linear E-i curve is b then at a given polarization, :

$$b_1 = \eta/i_1$$

and similarly

$$b_2 = \eta/i_2$$

Thus

$$b_1/b_2 = i_2/i_1$$

If η is a linear function of i, then

$$\eta = J i (p_{O_2})^{-1/2}$$

or

$$\log \eta = \log i - \frac{1}{2} \log p_{O_2} + \log J$$

Data illustrating this equation are shown in figure 10.

CONCLUSIONS

Data have been presented to show the effect of oxygen partial pressure on the polarization and maximum current of partially immersed flat-plate cathodes. It has been proven that polarization - oxygen partial pressure dependence for the flat-plate electrodes is valid for complex porous structures as well. A marked decrease in electrode polarization was observed at the lower range of p_{O_2} studied (0.1 to 1.0 atm). Beyond this range the polarization decrease is not as marked. Therefore extremely high p_{O_2} values are ineffective in obtaining minimum cathode polarization for practical fuel cell operation.

The following equations are very useful for predicting cathode currents under different operating conditions if the cathode current is known for one condition, and there are no other experimental data available.

$$\left(\frac{i_{E,1}}{i_{E,2}} \right) = \left(\frac{C^*_1}{C^*_2} \right)^{1/2}$$

$$\left(\frac{i_{E,1}}{i_{E,2}} \right) = \left(\frac{p_{O_2,1}}{p_{O_2,2}} \right)^{1/2 \dagger}$$

These equations are valid for complex porous structures only when:

1. The activation polarization is small.
2. Diffusion (both ionic and gaseous) limitations and electrical resistance of the structure are negligible.

The difficulty in defining the three-phase interface is complicated by the presence of oxides and uneven surfaces. For this reason we obtain reproducible current densities by expressing them in μA per linear centimeter of the interface. In order to prevent disturbance of the interface, the electrolyte was not stirred while measurements were taken.

Since the relationship $i_E \propto (p_{O_2})^{1/2}$ exists at all electrodes involving interphase transport of O_2 (gas/liquid), it seems likely that interphase transport is the mass transfer rate controlling mechanism.

\dagger Used when the same KOH concentration is used

APPENDIX

PO_2	=	partial pressure of O_2 (atm)
i_E	=	maximum obtainable current on a half-immersed flat-plate electrode that results from the electro-reduction of O_2 (μ A/cm meniscus length)
N	=	number of moles of O_2 diffusing per unit area - unit time
D	=	diffusivity coefficient (unit area/unit time)
δ	=	mean length diffusion path in the meniscus
ΔC	=	difference in O_2 concentrations between that at the gas/liquid and liquid/solid interfaces in the meniscus (moles of O_2 /unit volume of electrolyte)
μ	=	viscosity
C^*	=	equilibrium concentration of O_2 in KOH electrolyte at a given PO_2 (ml stp of O_2 /liter of electrolyte)
A	=	proportionality constant
J	=	proportionality constant
b	=	slope of linear E-i curve
η	=	polarization (volts)

LITERATURE CITED

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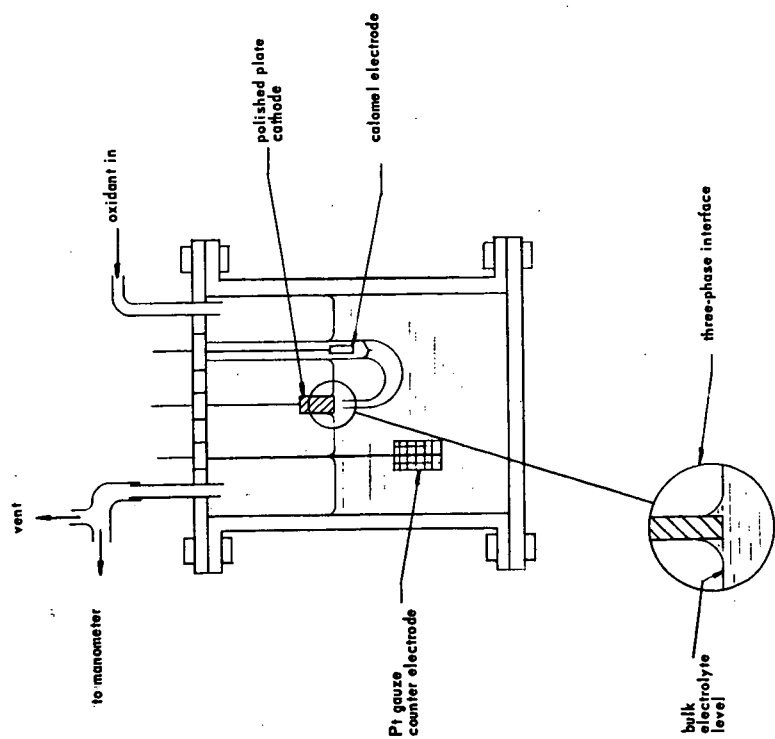


Figure 1 - Experimental Arrangement

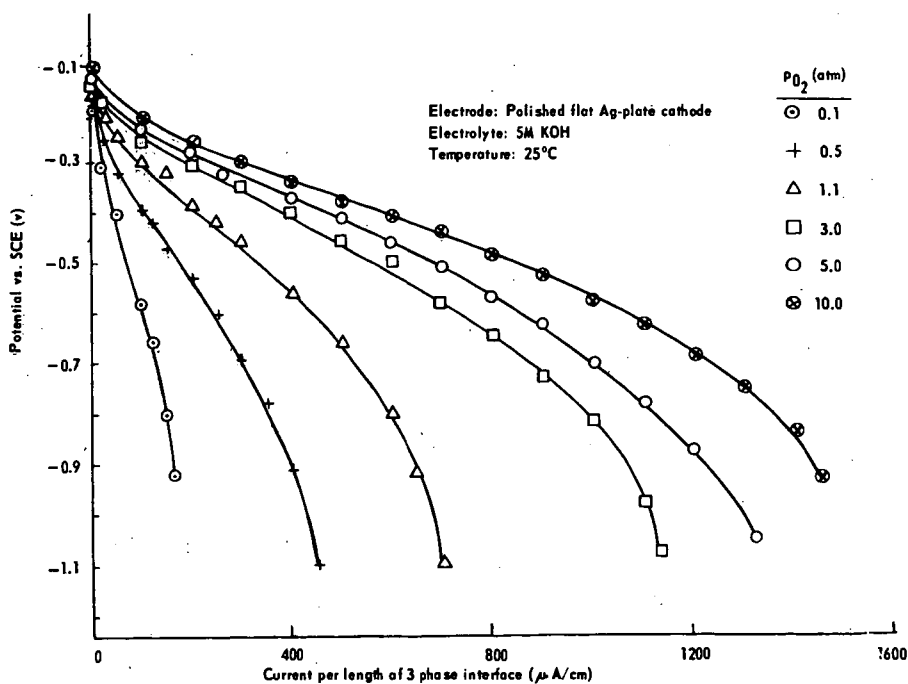
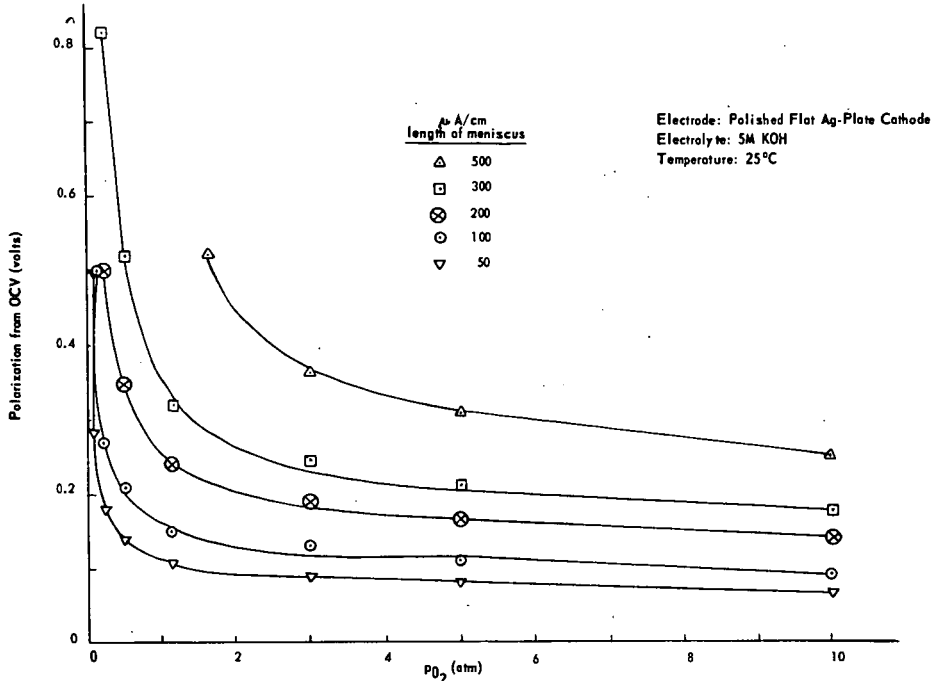
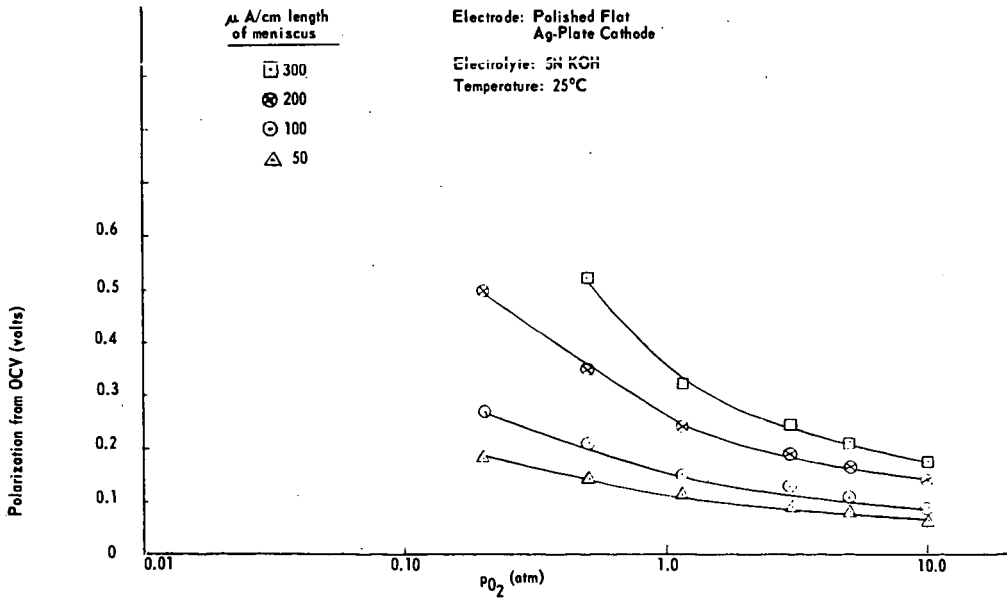


Figure 2 - Polarization of Flat-Plate Electrode Partially Immersed in KOH Electrolyte

Figure 3 - Polarization from OCV vs. pO_2 for a Flat-Plate Electrode Partially Immersed in KOH ElectrolyteFigure 4 - Polarization from OCV vs. pO_2 for a Flat-Plate Electrode Partially Immersed in KOH Electrolyte

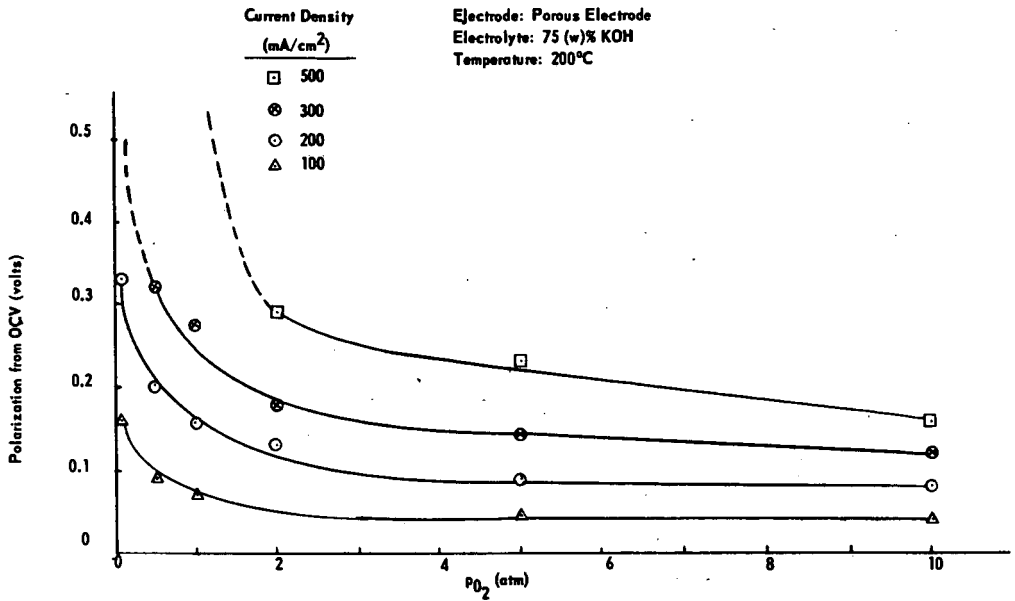


Figure 5 - Polarization vs. pO_2 for Complex Porous Structures

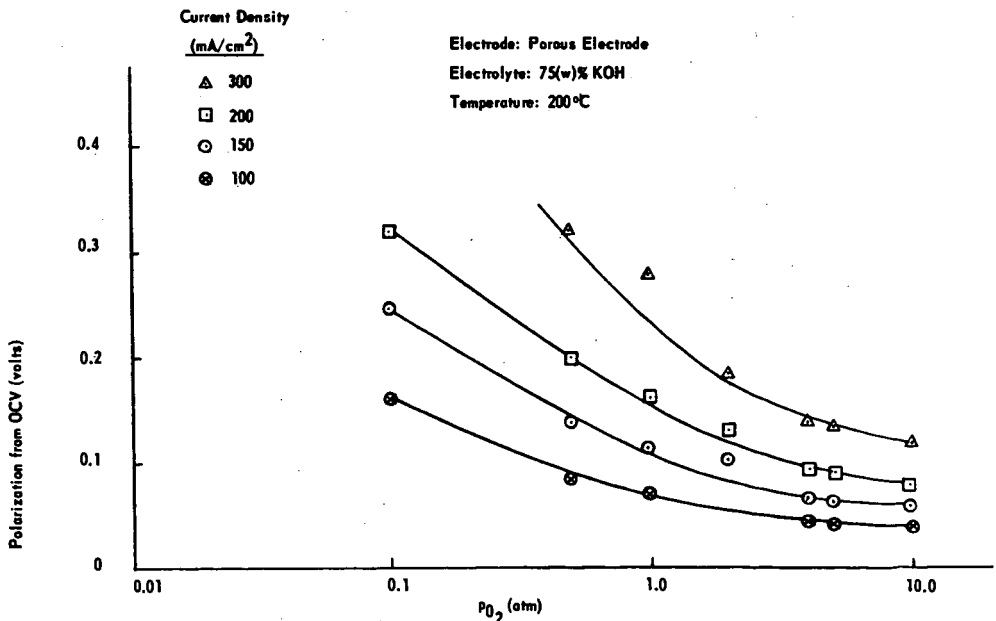
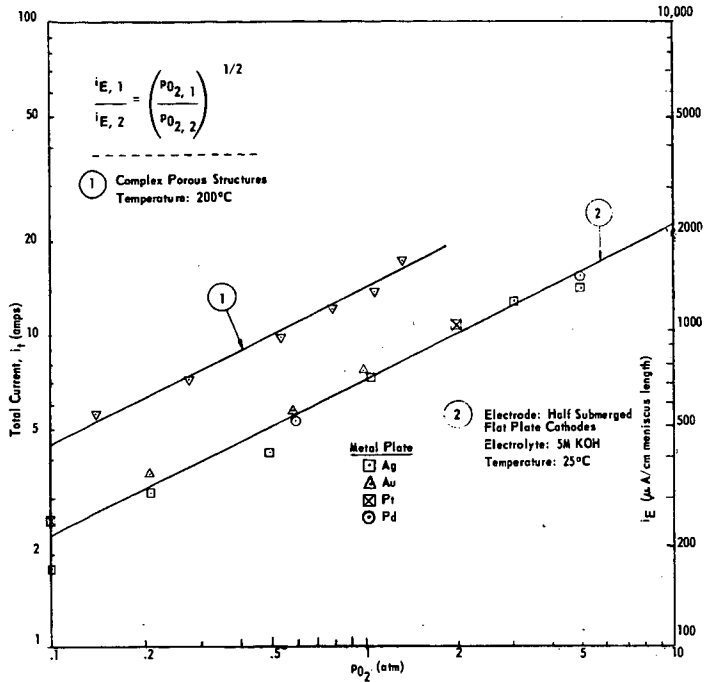
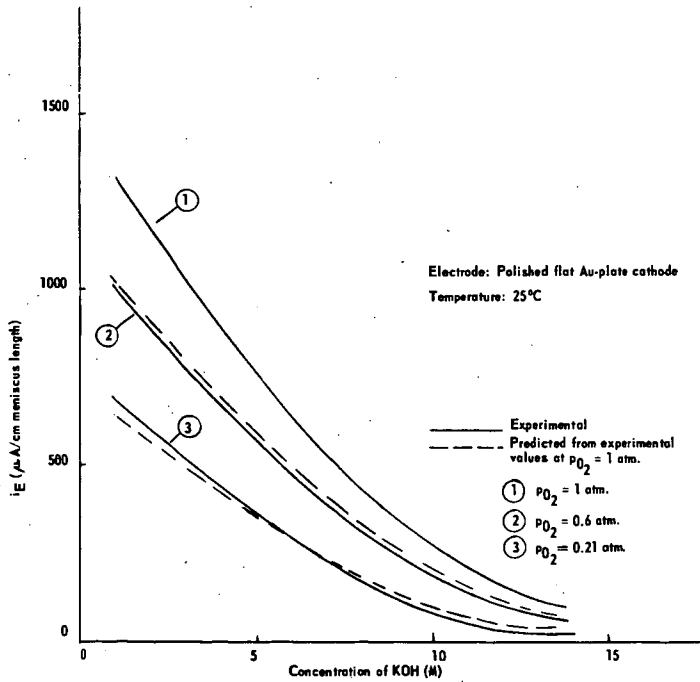
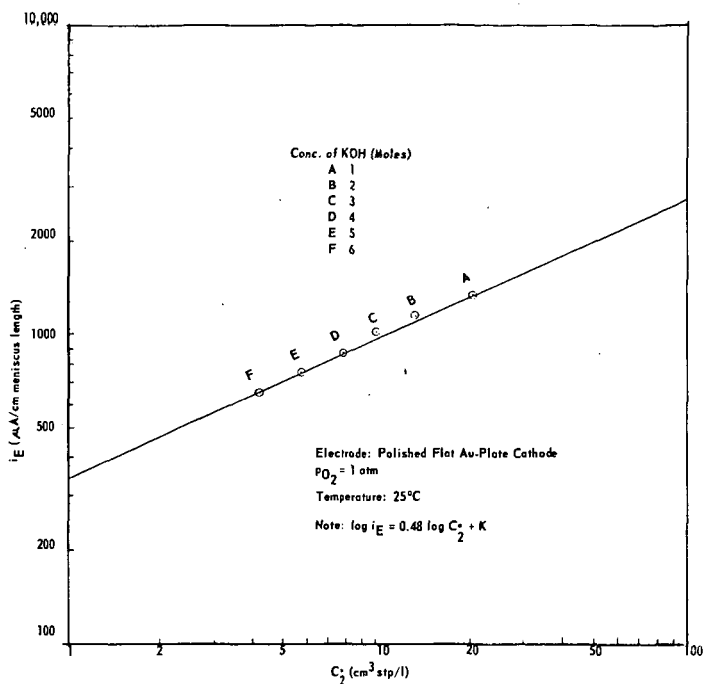
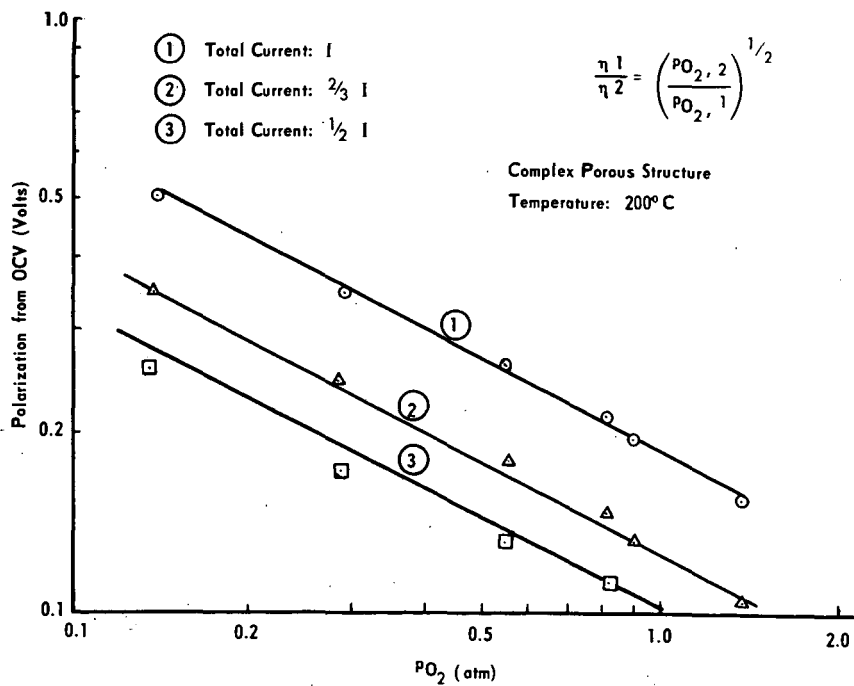


Figure 6 - Polarization vs. pO_2 for Complex Porous Structures

Figure 7 - iE vs. pO_2 for Various ElectrodesFigure 8 - iE vs. Concentration of KOH for a Flat-Plate Electrode

Figure 9 - i_E vs. C_2 for Flat-Plate ElectrodeFigure 10 - Polarization vs PO_2